Unique Structures of Nanoconfined Liquid Crystals Doped with Photoinduced Charge Transfer Compounds

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Introduction

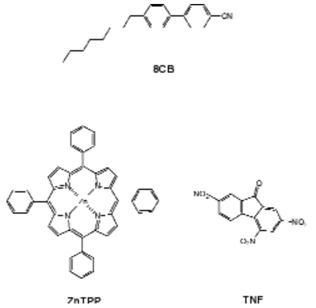
Photosynthetic proteins have complex relaxational processes that span the range of picoseconds to seconds. This unusually wide temporal range of dielectric relaxation of proteins is recognized as an important contributor to efficient charge separation in natural photosynthesis.[1,2] It enables the protein environment in reaction centers to act as a "solvent" that can reorganize to produce an optimized free energy for each charge separation step. An interesting class of solvents that mimic the broad temporal responses of protein relaxation are liquid crystals. Nematic and smectic liquid crystals possess an unusually wide range of dielectric reorganizational responses that range from picoseconds to microseconds and are thus separated from the more homogeneous responses of conventional isotropic liquids.

It is also known that confinement of liquid crystals on 100 nm length scales or less can lead to new structural characteristics and a range of dielectric responses that are extended by orders of magnitude.[3] Thus, confined nanodomains of liquid crystals represent unique biomimetic environments for the study of photoinduced electron transfer reactions. Optimal confinement configurations are sought that will produce structural and dynamical properties leading to efficient charge separation and vectorial charge transport for photochemical energy conversion.

Methods and Materials

The smectic liquid crystal, 4′-octyl-4-biphenylcarbonitrile (8CB), was used in various confinement configurations and is illustrated in Fig. 1. 8CB is a well known liquid crystal that forms a lamellar structure with an interlayer spacing of 31.4 Å, ideal for small angle x-ray scattering (SAXS) studies. It provides a measure of the degree of alignment of the liquid crystal and also any photoinduced structural changes. Also shown in Fig. 1 are the photochemically active dopants used, a Zn tetraphenyl porphyrindonor (ZnTPP) and a 2,4,7-trinitrofluorenone (TNF) acceptor.

FIG. 1. The smectic liquid crystal (8CB) and the photochemically active dopants (ZnTPP and TNF).



The confinement matrix used was nanoporous anodic aluminum oxide (AAO), synthesized by Professor J. Xu's group at Brown University. An AFM image of the unusually homogeneous AAO sample is shown in Fig. 2. The pores are ~50 nm in diameter and thus have a very high aspect ratio. Capillary action is used to draw the liquid crystal into the pores.

Results

Large structural changes are observed in the pure 8CB liquid crystal vs. doped liquid crystals when under nanoconfinement, while no structural changes are observed in bulk samples. The results can be summarized by Fig. 3, showing the diffraction peaks at Q values of 0.16 and 0.51 Å^{-1}, in addition to the diffraction peak at 0.21 Å^{-1} present in pure 8CB. Furthermore, the data show that 8CB molecules are aligned parallel to the pores and that the dopants are also similarly well aligned.

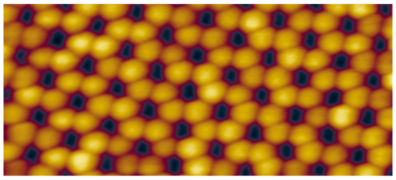


FIG. 2. An AFM image of AAO, with pore diameters of ~50 nm.

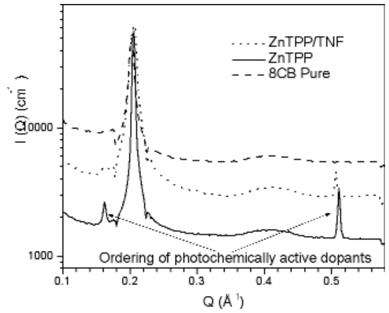


FIG. 3. The SAXS data for pure and doped 8CB in nanoporous AAO.

Discussion

The data indicate that the photochemically active chromophores are structurally ordered under confinement, while randomly oriented in the bulk. Interestingly, the highest Q diffraction at 0.51 Å^{-1} corresponds to the approximate diameter of the ZnTPP molecule. Structural ordering of the chromophores as a result of the AAO matrix and the liquid crystal solvent increases the likelihood of achieving vectorial, photoinduced charge separation.

Acknowledgments

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